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Preparation, photoluminescent properties and quantum size effect of ZnS nanoparticles @ mesoporous silica CMI-1

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Abstract

ZnS nanoparticles @ the channels of a mesoporous silica CMI-1 have been prepared by using a quite simple method and their photoluminescent properties have been studied. Characterization results confirm the presence of ZnS inside the material. PL spectrum of the nanocomposite shows an excitonic emission from bulk ZnS while an important blue-shifted emission attributed to quantum size effect of extremely small ZnS nanoparticles is also revealed. These interesting photoluminescent properties have been correlated with the surface modification and the interaction between ZnS nanoparticles and mesoporous surface. The present findings should lead to potential applications in optoelectronics and help to design the light-emitting systems and laser generators.

1. Introduction

The new design of light-emitting nanomaterials based on semiconductor of nanometric size is a current and important research topic and has led to a great number of researches about the conception of optoelectronic nanocomposites [1]. It is known that the enhancement of the semiconductor band gap due to quantum size effect can be achieved when the semiconductor particle size reaches the Bohr radius. The only way to prepare such nanoparticles is to limit their growth at the beginning of their formation. Therefore scientists have tried various capping methods to decrease the polydispersity of nanoparticles, to control the particle size and to enhance their stability using micelles [2], reverse micelles [3], polymers [4], zeolites [5] and sol–gel method [6] ...

Mesoporous materials [7] with pore size ranging from 2 to 10 nm have been used as a new type of host for the encapsulation of polymers [8], organic molecules [9] and semiconductor particles [10]. These new materials have very good properties such as large surface area (>1000 m^2/g) and pore volume (>1.4 cm^3/g), tunable pore diameter (2–10 nm), hexagonal structure, thermal stability, which make them ideal hosts for the growth of semiconductor nanoparticles. Interestingly, contrary to MCM-41 type mesoporous materials prepared by using cetyltrimethylammonium bromide as surfactant, highly ordered mesoporous CMI-1 materials [11] showed the absence of the emission at 1.9 eV [12] which is crucial for the optoelectronic composites and for the laser system design. This important characteristic of CMI-1 mesoporous silica has been attributed to the presence of less defect sites due to the mild synthesis conditions and the soft surfactant removal method.

Zinc oxide (band gap = 3.37 eV) has been widely studied due to its potential applications such as varistors [13], gas sensors [14,15], electrical and optical devices [16] and laser sources [17]. Our recent studies have evidenced very interesting photoluminescent properties and quantum size effect of ZnO nanoparticles confined inside nanocages of Faujasite zeolites and nanochannels of highly ordered

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mesoporous silica CMI-1 [18,19]. Surprisingly and for the first time, a strong Random Lasing effect arising from one and even two photon excitation process was revealed when submitting nanocomposites ZnO/CMI-1 to a 3.66 eV (slightly higher than the band gap of ZnO) or a 1.82 eV (half the band gap of ZnO) femtosecond incident beam [19]. This important observation can generate high interest in design of short wavelength lasers, blue-light emitting diodes, UV detectors or in the conversion of long to shorter wavelengths.

ZnS is also a wide band gap semiconductor (3.66 eV) and is commonly used as phosphor in panel displays, in thin film electroluminescent devices and in photocatalysis [20,21]. The preparation of nanosized ZnS particles is of particular interest due to their potential excellent optical and optoelectronic properties, however, only a few number of papers related to ZnS nanoclusters can be found in the literature due probably to the difficulty in their preparation since there is no chemical precursor which can give directly ZnS particles. It is thus still a great challenge to generate ZnS nanoparticles into the channels of porous media.

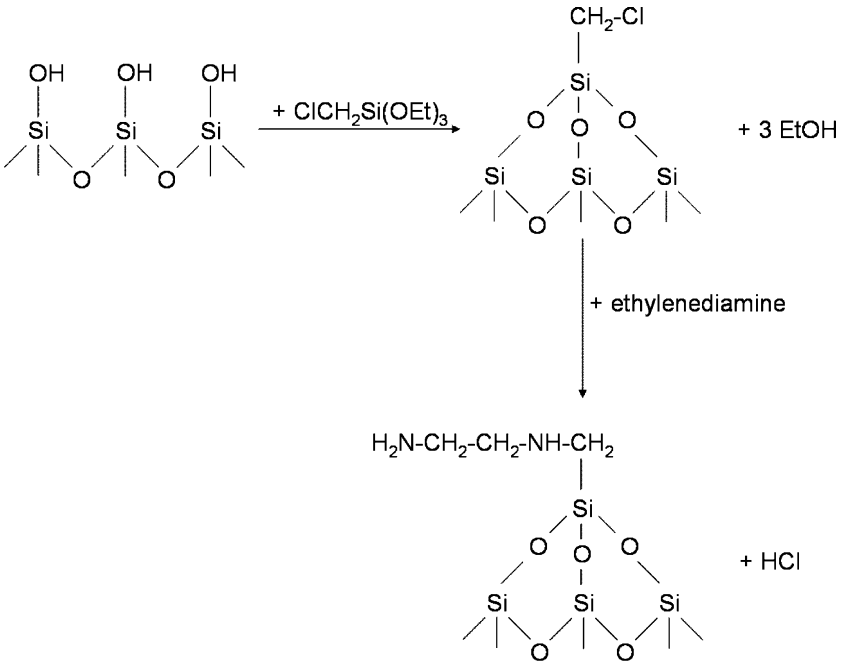
In this work, we report a simple method to prepare nanocomposites made of ZnS nanoparticles @ mesoporous material CMI-1. The method implies surface modification with ethylenediamine groups and growth of ZnS nanoclusters. The photoluminescent properties and quantum size effect of the obtained materials have been studied.

2. Experimental

The mesoporous matrix CMI-1 was prepared as described elsewhere [11]. Functional groups (chloromethyl and ethylenediamine groups) were introduced to the pore surfaces of mesoporous silica CMI-1 by refluxing the mixture of calcined CMI-1 with chloromethyltriethoxysilane (CMTS, 1 g of CMI-1 for 0.85 g of CMTS) and ethylenediamine (ED, 0.24 g of ED) in 60 ml of dry toluene under a nitrogen atmosphere for 8 h. The ethylenediamine (ED) groups have been anchored on the internal surface of the mesochannels following the reactions represented in Scheme 1. The samples were washed several times with toluene and ethanol to remove the products of the reaction and were dried at 80 °C during 12 h.

In order to introduce ZnS nanoparticles inside the channels of the mesoporous material CMI-1, the incipient wetness method [22] was employed. 0.5 g of the CMI-1 sample was wetted in 20 ml of a 0.1 M zinc acetate aqueous solution during 1 h under stirring (300 rpm). After drying, the resultant was calcined at 150 °C in the flow of H_2S during 6 h. The obtained sample is labeled as ZnS-ED-CMI-1 and contains 10% wt. in ZnS.

Nitrogen adsorption–desorption isotherms were carried out at −196 °C over a wide relative pressure range from 0.01 to 0.995 with a volumetric adsorption analyzer TRISTAR 3000 manufactured by Micromeritics. The sample was degassed further under vacuum for several hours at room temperature before nitrogen adsorption measurements. The pore diameter and the pore size distribution were determined by the BJH (Barret, Joyner, Halenda) method [23]. Wide-angle XRD measurements were taken with a Siemens D-5000 diffractometer and Small-angle XRD patterns were recorded with a Panalytical X'Pert diffractometer, both of them being equipped with a copper anode producing X-rays with a wavelength equal to 1.54178 Å. Photoluminescence spectra were recorded at room temperature with an ArF laser (193 nm) as the



Scheme 1. Ethylenediamine (ED) groups anchoring at the internal surface of mesochannels.

excitation source and an iCCD camera as the detector. The laser beam was focused onto the sample with a spot size of 1.36×10^{-2} cm^2.

3. Results and discussion

Fig. 1 compares the isotherm curves and the pore size distributions of the as-prepared CMI-1 material, the surface modified ED-CMI-1 material and the ZnS-ED-CMI-1 nanocomposite. The results are summarized in Table 1. The decrease in BET surface area, pore diameter and pore volume after the surface modification process indicates that the anchoring of ED groups was successfully realized. The further decrease of surface area and pore volume after the growth of ZnS provides indirect evidence that ZnS nanoparticles are formed inside the channels of ED-CMI-1 material. The pore diameter of the samples ED-CMI-1 and ZnS-ED-CMI-1 remains constant, which means that the mesoporous channels of CMI-1 are still accessible after the growth of ZnS. The shape of the three isotherm curves being the same, the mesoporosity is thus well conserved during the functionalization step and the formation of ZnS nanoparticles inside the ED-CMI-1 material.

XRD patterns within the 2θ range of 1.0°–5.0° for CMI-1, ED-CMI-1 and ZnS-ED-CMI-1 are presented in Fig. 2. The unit cell parameter a_0 and the values of d_{100} are listed in Table 1. All of these XRD patterns display three peaks at low angle range with a quite intense reflection and two other relatively weak diffraction lines. These three diffraction lines can be indexed in a 2D hexagonal symmetry (P6 mm) indicating the very good quality of our samples and that the hexagonal order was retained after the growth of ZnS nanoparticles. From the values of d_{100}, inter-reticular distances, we can determine the unit cell parameter a_0. As a_0 represents the sum of the pore diameter and the wall thickness [11] and because the pore diameter remains constant during the ZnS formation, it is obvious that the framework of CMI-1 materials has been subjected to some slight contraction during the growth of ZnS inside its channels. The relative low intensity of three diffraction lines is due to the presence of ZnS nanoparticles (10% wt) @ surface modified mesoporous silica ED-CMI-1.

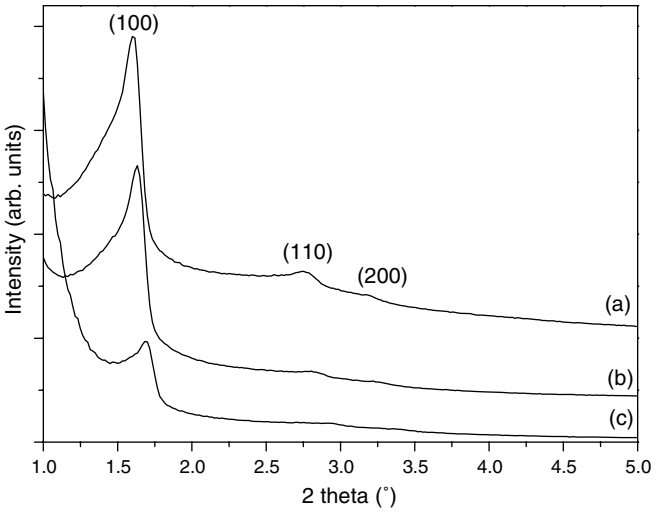


Fig. 2. XRD patterns at low angle ranges of samples CMI-1 (a), ED-CMI-1 (b) and ZnS-ED-CMI-1 (c).

In the large scale region ($4° < 2\theta < 60°$, Fig. 3), the XRD pattern of CMI-1 material shows a broad reflection in the

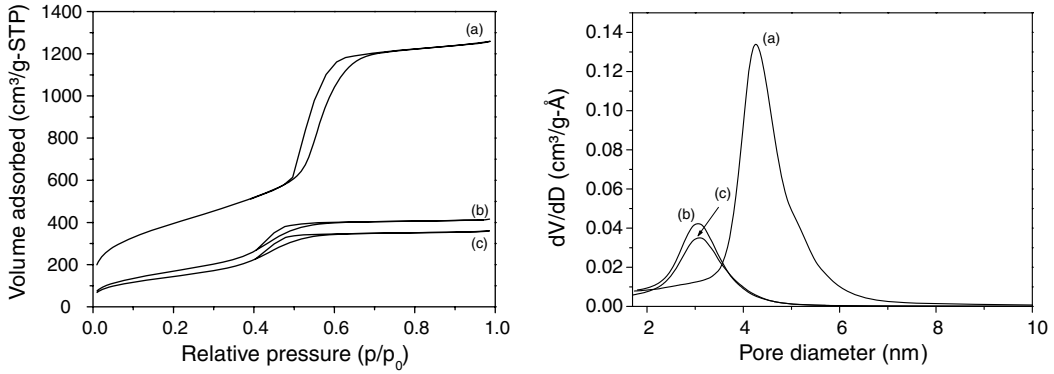


Fig. 1. Nitrogen adsorption–desorption analysis for the samples CMI-1 (a), ED-CMI-1 (b) and ZnS-ED-CMI-1 (c).

Table 1
Nitrogen adsorption–desorption and XRD results of the samples CMI-1, ED-CMI-1 and ZnS-ED-CMI-1

	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	d_{100} (nm)	a_0 (nm)	ZnS (wt%)
CMI-1	1442	1.80	4.2	5.5	6.4	–
ED-CMI-1	644	0.56	3.1	5.4	6.3	–
ZnS-ED-CMI-1	541	0.49	3.1	5.2	6.0	10

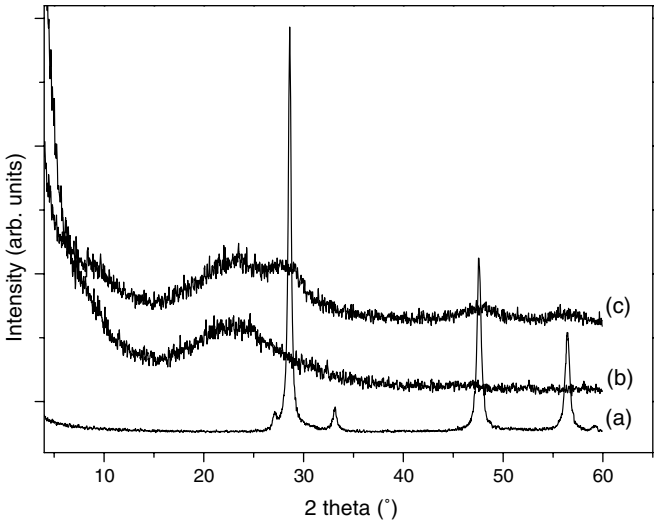


Fig. 3. XRD patterns at wide angle ranges of bulk ZnS (a), CMI-1 (b) and ZnS-ED-CMI-1 (c).

zone of 15–30° (2θ) due to the amorphous structure of the mesoporous walls (Fig. 3b). On the other hand, in the XRD pattern of the nanocomposites (Fig. 3c), three broadened and very weak peaks appear in addition to the broad peak of CMI-1 material. By comparison with the XRD pattern of pure ZnS powder (Fig. 3a), these three peaks are attributed to the crystal structure of the ZnS nanoparticles and, according to the Scherrer formula, the average size of the ZnS crystallites can be estimated to be 3.4 nm (on the basis of the FWHM of the broadened peak). This is quite in agreement with the results obtained by nitrogen adsorption–desorption analysis about the pore diameter (3.1 nm). This means that using well defined pore diameter of mesoporous silica CMI-1, we can control the particle size of the semiconductor and limit the growth of the particles of the semiconductor.

Fig. 4 depicts the photoluminescent spectra of the ED-CMI-1 (a) and the ZnS nanoparticles@ED-CMI-1 (b). The analysis of the spectrum has followed the same method developed in our laboratory [18,19]. The best fit of the experimental curves was given by using three Gaussian functions whose characteristics can be found in Table 2. Our recent PL studies on pure CMI-1 and water-treated CMI-1 mesoporous silicas showed two PL bands at 2.94 and 3.9–4.0 eV which can be attributed to surface defects associated with silanol groups which give rise to E'-centers ($\equiv Si^{\bullet}$) and $\equiv Si-O_2^{\bullet}$, respectively, after a dehydroxylation process via calcinations [12]. It was also observed that the calcination in O_2 favors the formation of E'-centers (2.94 eV) while water treatment and then calcination in Oxygen enhances the direct formation of $\equiv Si-O_2^{\bullet}$ centers from silanol groups and the PL band was slightly shifted from 3.89 to 4.0 eV. Thus, the PL bands at 3.0 and 4.0 eV observed on ED-CMI-1 (Fig. 4a) can be attributed to E'-centers ($\equiv Si^{\bullet}$) and $\equiv Si-O_2^{\bullet}$ centers, respectively. As observed in CMI-1, the intensity of the PL band due to E'-centers predominates over that from $\equiv Si-O_2^{\bullet}$ centers

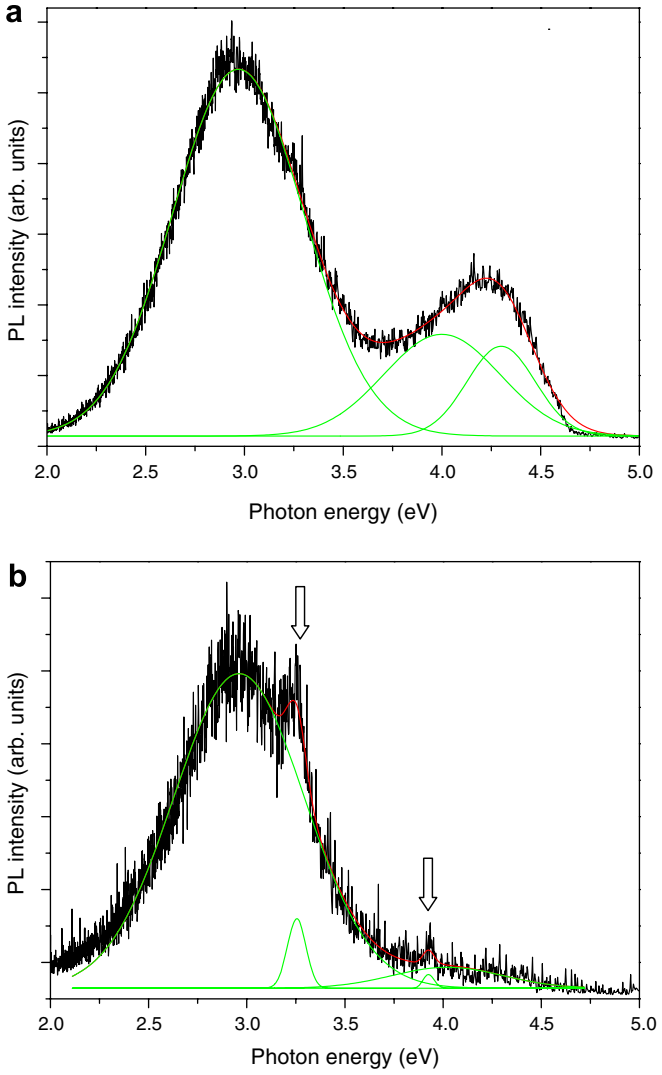


Fig. 4. PL spectra of the ED-CMI-1 modified material (a) and the ZnS-ED-CMI-1 nanocomposite (b) (excitation = 193 nm, 6.4 eV).

Table 2
Positions, full widths at half maximum (FWHM) and areas for the observed luminescence peaks

	Position (eV)	FWHM (m eV)	Area (%)
ED-CMI-1	3.0	660	73.0
	4.0	580	18.0
	4.3	340	9.0
ZnS-ED-CMI-1	3.0	660	91.6
	3.25	80	2.9
	3.9	30	0.3
	4.0	560	5.2

and the surface functionalization by ethylenediamine groups did not change the ratio in intensity between two PL bands (at 3.0 and 4.0 eV). Although the PL band at 4.3 eV was previously assigned by Skuja et al. [24] and Stathis et al. [25] to E'-centers, it is still unclear at the moment on its origin. We believe that this PL band could also be

associated with silanol groups, but different from E'-centers (at 3.0 eV).

The PL spectrum of ZnS-ED-CMI-1 nanocomposite is given in Fig. 4b and the characteristics of the corresponding four gaussian functions are listed in Table 2. Firstly, we observe the vanish of the PL band at 4.3 eV after the formation of ZnS nanoparticles inside the channels of ED-CMI-1. If we attribute the origin of this PL band to surface defects associated with silanols groups (Si–OH), its extinction is very probably due to the interaction between ZnS nanoparticles and the surface of the mesochannels. The PL band at 3.0 eV is certainly induced by E'-centers. The PL band at 4.0 eV ($\equiv$Si–$O_2^{\cdot}$) did not completely disappear but its relative intensity has dramatically decreased.

It is worthy to note that the ZnS nanoparticles are formed by the reaction of ZnO initially formed by the decomposition of $Zn(CH_3COO)_2$ inside the ED-functionalized mesochannels during a flow of H_2S at 150 °C. Our previous study on the PL properties of ZnO@mesoporous silica CMI-1 showed that after the introduction of ZnO nanoparticles inside the channels of the mesoporous silica (by decomposition of $Zn(NO_3)_2$ at 500 °C under O_2), the ratio in intensity between the PL bands at 2.7 (3.0 in this work) and 3.9 eV remains unchanged. The sharp decrease in intensity of the PL band at 4.0 eV compared with that at 3.0 eV is therefore very probably due to the interaction between ZnS and $\equiv$Si–$O_2^{\cdot}$ centers or due to the decrease in the number of $\equiv$Si–$O_2^{\cdot}$ centers in the presence of a H_2S flow. As the temperature is increased, $\equiv$Si–$O_2^{\cdot}$ can be converted to E'-centers by the reaction $\equiv$Si–$O_2^{\cdot} \rightarrow \equiv Si^{\cdot} + O_2$. This is why the ratio in intensity between PL bands at 3.0 eV (E'-centers) and at 4.0 eV ($\equiv$Si–$O_2^{\cdot}$) increases sharply. However, all the conclusions of this kind need further studies.

In addition, the PL spectrum of the nanocomposites displays two very narrow and evident peaks located at 3.25 and 3.93 eV (indicated by arrows). The first one arises of course from the recombination of excitons in ZnS nanoparticles with a large but monodisperse particle size. The second PL peak is obviously attributed to quantum size effect of extremely small ZnS nanoparticles. The width of this peak indicates that the size distribution of the small ZnS nanoparticles is very narrow. According to Brüs equation, the particle size is estimated to be 3.6 nm ($\Delta E = 680$ meV).

The particle size obtained by Scherrer relation (3.4 nm) is in quite good accordance with the one obtained by Brüs equation (3.6 nm).

The presence of two excitonic emissions in PL spectrum can be correlated with the heterogeneous functionalization of internal surface of mesochannels. ZnS nanoparticles with two different particle sizes, one of which could be much higher than that of Brüs particle size. The present findings should lead to potential applications in optoelectronics due to the size-dependent optical properties as a result of quantum size effect and help to design the light-emitting systems and laser generators.

4. Conclusion

The growth of ZnS nanoparticles @ the channels of modified CMI-1 material has been successfully realized by using the surface modification method. The prepared ZnS-ED-CMI-1 nanocomposite was characterized by a series of techniques and the results of PL spectra demonstrate the expected quantum size effect arising from the extremely small size of the confined ZnS nanoparticles. The high efficiency of this simple method for the preparation of nanocomposites can be attributed to the versatility of CMI-1 materials as hosts for encapsulating guest materials.

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